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TECHNICAL FIELD

This invention relates to new process designs referring to permeable reactors (so called permreactors or membrane reactors) and to consecutive separators, including membrane type permeators, for conducting mainly the hydrocarbon steam reforming, hydrocarbon carbon dioxide reforming, combined hydrocarbon steam and carbon dioxide reforming, alcohol steam reforming, water gas shift, paraffin dehydrogenation, methanol synthesis, methane oxidation, and combination of these carbon fuel conversion reactions for the production of valuable upgraded fuels and chemicals. The invention also relates to the utilization of the end reaction products such as pure hydrogen and synthesis gas (hydrogen and carbon monoxide, hydrogen and carbon dioxide mixtures), and mixtures of these, into specific applications such as consecutive fuel cells, gas turbines, gas engines and synthesis reactors by application of uniquely presented process configurations.

BACKGROUND OF THE INVENTION

The current invention describes new and improved processes which involve permeable reactors (permreactors, membrane reactors) and downstream separators (including permeators) for the hydrocarbon-steam reforming, hydrocarbon-carbon dioxide reforming, combined hydrocarbon steam and carbon dioxide reforming, alcohol steam reforming, the water gas shift reaction, dehydrogenation reactions of alkanes (paraffins) and alcohols, hydrogenation reactions of alkenes to alkanes and aldehydes, ketones to alcohols, methane oxidation, and combination of these previous reactions.

The reactions and heats of reactions that are referred to and utilized within the embodiments of the invention are well known and are listed below:

$CH_4 + H_2O = CO + 3H_2$ (ΔH°_{298}=206.1kJ/mol), methane-steam reforming (1)

$CH_4 + CO_2 = 2CO + 2H_2$ (ΔH°_{298}=247.3kJ/mol), methane-CO_2 reforming (2)

$CO + H_2O = CO_2 + H_2$ (ΔH°_{298}=-41.15kJ/mol), water gas shift (3)

$C_nH_{2n+2}=C_nH_{2n} + H_2$ (endothermic dehydrogenation reactions, heat of reaction varies depending on the type of feedstock (alkane) processed in the reactor, e.g., ethane, propane, butane, pentane) (4)

$CO + 2H_2 = CH_3OH$ (ΔH°_{298}=-128.2kJ/mol), methanol synthesis (5)

$CO_2 + 3H_2 = CH_3OH + H_2O$ (ΔH°_{298}=-49.5kJ/mol), methanol synthesis (6)

$CH_3OH + H_2O = CO_2 + 3H_2$ (ΔH°_{298}= 49.5kJ/mol), methanol-steam reforming (7)

$RCH_2OH = RCOH + H_2$ dehydrogenation of alcohols to aldehydes (8)

$RCHR'OH = RCOR' + H_2$ dehydrogenation of alcohols to ketones (9)

$CH_4 + 1/2O_2 \dashrightarrow CO + 2H2$ (ΔH^o_{298}= -36.0kJ/mol) partial oxidation of methane (10)

Hydrogenation reactions of alkenes to alkanes, aldehydes to alcohols, and ketones to alcohols are the opposite of reactions (4), (8) and (9) respectively.

The aforementioned are catalytic reactions utilizing catalysts such as nickel (Ni), ruthenium (Ru), rhodium (Rh), rhenium (Re), palladium (Pd), platinum (Pt), iridium (Ir), chromium (Cr), copper (Cu), zinc (Zn), cobalt (Co), gold (Au) and other metals, and bimetallic catalyst compositions of these metals. The catalysts are supported on oxides of alumina (Al_2O_3), titania (TiO_2), silica (SiO_2), zirconia (ZrO_2), lanthanum (La_2O_3) and other metal supports, and are enriched with earth metals such as calcium (Ca), lanthanum (La), sodium (Na), potassium (K), magnesium (Mg), manganese (Mn) to reduce the deposition of carbon on the precious metal catalysts and prevent their loss of activity.

Use of related processes involving catalytic reactor with downstream permeator configurations and systems of those were disclosed in our previous US patent # 6,090,312 (July 2000). Use of these reactor-separator systems increase the overall process efficiency by increasing the total conversion of feedstocks such as the following: natural gas, landfill gas, coal gas, hydrocarbons, hydocarbons-CO_2 mixtures, methane, methane-CO_2 mixtures, alcohols. Moreover, the yields to hydrogen and carbon monoxide or hydrogen and carbon dioxide are increased by the use of the integrated membrane type permeators which separate effectively the H_2 and CO_2 gas constituents out of the reformed streams. Process efficiency is further improved by the recycling of unreacted and non-separated (non-permeated) hydrocarbons (e.g., methane) and carbon monoxide into the first (primary) reactor (reformer) or by the alternative direction of the same streams into a consecutive catalytic reactor (reformer or water gas shift reactor) for additional production of hydrogen and carbon dioxide. Direct utilization of the produced and separated hydrogen, synthesis gas, and hydrogen-carbon dioxide mixtures from these processes into consecutive synthesis reactors, fuel cells and gas turbines and engines are additional advantages and continuing applications and utilizations of the proposed processes.

Current invention and described processes elaborate on the substitution of the primary conventional reactor (i.e., reformer, water gas shift, dehydrogenation reactor) by a permeable (membrane-type) reactor (so called permreactor for simplicity) of specific design, and the correspondingly derived improved process operations and permeable reactor-separator configurations for the above mentioned reactions. Moreover, the introduction and specification of double wall type membrane reactors (double wall permreactors) offer a variety of processes related to the above reactions which can be implemented accordingly as described below.

A specific problem in parallel gas separation and reaction within microporous membrane reactors (permreactors) is the lack of selective separation for the target compound (e.g., hydrogen) in certain materials. Thus, microporous inorganics, polymers,

carbons and composites allow the permeation through the membrane of not only the targeted compound but also of other reaction products and reactants that compete for permeation based on their molecular diameter or molecular weight. This effect, separates in the permeate of the membrane reactor a stream which is not pure but needs further separation in order to be utilized as a pure compound (e.g., hydrogen for synthesis or fuel). Therefore, capital and operation costs are increased when a single wall membrane reactor of the above structure is to be used in the process. The introduced double wall permreactor solves this problem by applying a second consecutive membrane which only separates the targeted compound. For hydrogen separation as an example, a second metal membrane made by palladium or palladium alloys can be used after the first microporous membrane, as described below.

The described permreactors are designed to consist of interconnected parts which can be readily taken apart, cleaned, serviced and assembled when service or maintenance is necessary. For the disclosed integrated reaction-separation systems specific applications are disclosed such as the utilization of the end products and/or of the permeated (separated) streams into consecutively placed synthesis reactors (including additional reforming or water gas shift reactors), gas turbines and engines, and various types of hydrogen and methanol based fuel cells and fuel cell systems.

Previous reactor and permeable reactor (membrane reactor) designs from the above cited references refer mainly to methane and methanol steam reforming reactions but not to carbon dioxide reforming, water gas shift and dehydrogenation reactions as the present invention also does. Moreover, previous inventions refer to processes occurring within a single reactor or permreactor or other reaction vessel instead of reactor-separator systems as the present invention describes. Present invention introduces processes which are based on double wall permeable reactors (double wall membrane reactors) for conducting mainly hydrocarbon and alcohol catalytic processing reactions. The double wall membrane reactors can be of various designs and be made by various appropriate materials as disclosed within the embodiments and claims of the invention. The catalytic reactors are adapted to specific process requirements in terms of setting values of key operating variables such as reaction temperature, pressure, space velocity, feed composition, catalyst composition and weight, in order to deliver final products (such as hydrogen and synthesis gas) in the required purity and throughput for the consecutive applications. Selection of such variables like temperature, pressure, and feed composition in the different compartments of the described membrane reactor system is also of significant importance. This is because an interconnection and synergetic activity between the various compartments occurs during operation with reaction and separation operations to occur at the same time. Moreover, flexibility in the selection of the double wall permreactor materials such as metals, inorganics, organics and composites, allows for the design of such multifunctional permeable reactors which separate and deliver specific species (such as specific gases) with the required purity and throughput to the consecutive applications. Flexibility in the selection of functional and specific permreactor wall materials for each process operation have also economic advantages. Current disclosed permreactor and separator vessels can utilize membrane materials selected from classes of metals, inorganics (porous or non-porous), polymers, carbons and carbonaceous materials, and composites. Therefore, the selection of less expensive

membrane materials and manufacturing techniques for a specific permreactor, permeator and overall process is available with the current invented designs and will affect (reduce) the cost of the overall process operation.

Present invention also teaches the direct utilization of end product streams to consecutive synthesis reactors, fuel cells, gas turbines and gas engines. Use of such low pollution energy systems with increased efficiency is of updated interest in utility, energy, chemical, automobile and environmental companies. Present invention focuses on converting and upgrading primary hydrocarbon feedstocks such as methane, natural gas, coal gas, refinery feedstocks such as naphtha, alcohol feedstocks such as methanol, ethanol and higher alcohols into higher calorific value hydrogen and carbon oxide mixtures. Also, it focuses on converting secondary and waste hydrocarbon feedstocks such as acidic natural gas, biomass gas, flue gas rich in CO_2 and CH_4 to same valuable end products. Therefore, present invention describes environmentally benign processes which abate and upgrade at the same time, among other feedstocks, otherwise waste gases to valuable hydrogen, synthesis gas, hydrogen and carbon dioxide mixture. In situ conversion of carbon dioxide containing hydrocarbon mixtures to alternative fuels and chemicals, and the subsequent mitigation of the carbon dioxide negative atmospheric and terrestrial greenhouse effect is considered an additional benefit from the implementation of this invention.

SUMMARY OF THE INVENTION

The present invention discloses processes which consist of double wall permeable reactors (permreactors) and systems of such advanced reactors with consecutively placed separators to perform specific process operations. These integrated chemical-mechanical systems offer operational advantages by conducting in-situ reactions, in comparison with single wall permeable reactors and conventional non-permeable reactors. Consequently, different double wall permreactor processes are disclosed. These are used in catalytic hydrocarbon and alcohol reforming, water gas shift, hydrocarbon and alcohol dehydrogenation and hydrogenation reactions. The first process comprises of a double wall permreactor which incorporates three concentric hollow cylindrical tubes with the two inner ones to be made by permeable (permselective) metal, inorganic, carbon, polymer or composite materials depending on the type of feedstocks used, the reactions and reaction conditions occurring, and the desired composition of the final exit streams. Heating tubes run through the most-inner cylinder which is also filled with the main catalyst to conduct the appropriate reaction. Additional catalyst can be placed in the two outer annular spaces created between most-outer and next-inner and between next-inner and most-inner tubes. By varying the catalyst position and catalyst type this process can be applied to a number of different reactions. Similarly, the second process involves a double wall permreactor which consists of three concentric hollow cylindrical tubes with the two inner ones to be made by permeable (permselective) metal, inorganic, carbon, polymer or composite materials and with the catalyst for the main reaction to be contained in the annular space between the most-outer and the next-inner cylindrical tubes. Heating in this process is applied into the external side of the most-outer tube. By

applying catalyst at the different annular spaces created between the concentric tubes, this process can be applied to various reactions. The two processes differ in the heat and mass transfer profiles and distribution across the radial distance and along the axial distance. Use of the described advanced permreactor processes offer significant increases in conversion of reactants and increases in yield and selectivity of products. This is achieved via improved mass and heat transfer, and improved reaction rates within the defined reactor (and catalyst) parts of the process as described above. Also, the effect of removing products out of the defined reaction zones during the reaction, increases the reactant conversion and the yield to useful products by shifting the equilibrium of the occurring reactions to the product side. Further, use of the described permreactors allows for systems of reactions to take place and be combined in the same module. Synergetic effets of utilizing products and/or reactants of these reactions to conduct improved processes in a consecutive or/and parallel manner is also a result of this invention.

Moreover, this invention pertains to combined processes of the described permreactors with consecutive permeators for the further separation and processing of the post-reaction gases exiting from the permreactors. Permeators can be made by polymer membranes for the concomitant separation of hydrogen and carbon dioxide gases or by metal, inorganics and carbon membranes for the separation of hydrogen only. These permreactor-permeator systems are applied to combined hydrocarbon steam and carbon dioxide reforming, hydrocarbon-steam reforming, hydrocarbon-carbon dioxide reforming, alcohol steam reforming, water gas shift, paraffin dehydrogenation, hydrocarbon, aldehyde, ketone hydrogenation reactions and methane oxidation. The processes are capable to increase the reactant conversion and the yield to hydrogen, carbon monoxide, and carbon dioxide. The separated hydrogen and carbon oxides can be used in consequent chemical synthesis reactions and as fuel in fuel cells, gas turbines and gas engines. The invention also includes hydrocarbon-CO_2-steam reforming process which consists of permreactors with cryogenic separators wherein the consecutive cryogenic separators replace permeators, and a pure mixture of hydrogen and carbon monoxide are recovered as final products. Similar permreactors as described above are directly interconnected with solid oxide fuel cells for using the products hydrogen, carbon monoxide and the unreacted steam as direct fuel in the anode of the cell. Further, the invention includes use of the disclosed permreactors in series with methanol synthesis and methanol reforming reactors for final production of methanol, hydrogen and carbon dioxide for use as further synthesis gases or as fuels. Further, the invention describes a dehydrogenation reaction in the middle annular space combined with the hydrogen permeation radially in the reactor via the metal membrane and the reaction of hydrogen with aldehydes or ketones in the adjacent sides of the reactor to yield alcohols, with the metal membrane to be used also as catalyst. Also, similar dehydrogenation reaction in the middle annular space is combined with hydrogenation and hydrogen reduction reactions in the adjacent spaces, such as a hydrocracking reaction of higher paraffins to yield lower paraffin and olefin products in a beneficial manner. Finally, a methane oxidation process is disclosed which uses oxygen transporting membranes to deliver oxygen into adjacent flowing methane streams for partial oxidation reactions which produce synthesis gas

(hydrogen and carbon monoxide). Detailed description of the invention are presented in the embodiments of the following Figures.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1, shows a view of a vertical cross section of a concentric double wall cylindrical permreactor with tubular type heaters located along the main catalyst zone, consisting of an inner metal, non-porous or porous inorganic, or composite membrane tube and an outer membrane tube made by metal, non-porous inorganic, composite or high temperature organic membrane enclosed within a far-outer impermeable tube.

Fig.2, shows a sectional view of the same permreactor as in Fig.1, including the three catalyst beds, the two cylindrical type inner and outer membrane tubes, and the inlet and outlet ports in each section of the permreactor.

Fig.3, shows multiple double wall permreactors of those described in Fig.1, but without the external impermeable tube, which are placed symmetrically inside a larger common metal tube, to create a multiple tube permreactor with a common external area for collecting final permeate hydrogen.

Fig.4, shows a cross section of a similar concentric double wall permreactor, consisting of an outer impermeable tube, a next-inner membrane tube made by metal, non-porous or porous inorganic, or composite membrane, and a most-inner membrane tube made by metal, non-porous inorganic, composite or high temperature organic membrane.

Fig.5, shows multiple double wall permreactors of those described in Fig.4, which are placed symmetrically inside a larger stainless steel tube, to create a multiple tube permreactor with a common external heating area.

In the Figures below, the permreactors are as those described in Fig.1 and Fig. 4 above.

Fig.6, shows a process which includes a catalytic permreactor and a consecutive permeator or optionally a system of two catalytic permreactors in series for hydrocarbon steam and CO_2 reforming or for hydrocarbon CO_2 reforming only. The reject from the permeator stream containing non-permeate hydrocarbon and CO can be optionally fed into a consecutive catalytic steam reforming reactor.

Fig.7, shows a similar process with this in Fig.6, in which the initial feedstock consists only of carbon monoxide (CO) and steam to undergo only the water gas shift reaction in the first catalytic permreactor. The reject from the permeator, CO stream, can be recycled into the first permreactor or optionally fed into a consecutive water gas shift reactor.

Fig.8, shows a process which includes a permreactor-permeator or a non-permeable reactor-permeator applied in the catalytic dehydrogenation of C_1-C_4 or higher alkane hydrocarbons; the permeate stream from the membrane permeator may consist of hydrogen or olefin depending on the type of membrane used for the separation. In the case which hydrogen permeates through the membrane, the reject from the permeator olefin rich stream can be used for polyolefin production in a consecutive reactor. In case

of olefin separation through the permeator, the reject paraffin rich stream can be recycled into the first permreactor.

Fig.9, shows a catalytic permreactor-permeator process for the hydrocarbon or alcohol steam reforming reaction. The reject from the membrane permeator hydrocarbon and carbon monoxide stream can be recycled into the initial reformer or fed into a consecutive (second) steam reforming reactor.

Fig.10, shows a system of a catalytic permreactor or non-permeable reactor process which combines a consecutive cryogenic separator for hydrocarbon steam and CO_2 reforming or for hydrocarbon CO_2 reforming only. The one liquified stream separated from the cryogenic separator, containing hydrocarbon, CO_2 and steam can be alternatively fed into the inlet of the initial reforming reactor. The gaseous stream from the separator contains H_2 and CO.

Fig.11, shows a process which includes a catalytic permreactor or non-permeable reactor for hydrocarbon steam and CO_2 reforming or hydrocarbon CO_2 reforming only with complete conversion of hydrocarbon and CO_2 gases in the reactor to H_2 and CO, which product mixture is fed directly into a SOFC (solid oxide fuel cell) unit for electricity generation.

Fig.12, shows a process which includes a catalytic permreactor for hydrocarbon, steam, and CO_2 reforming or hydrocarbon CO_2 reforming only with a consecutive methanol synthesis reactor from hydrogen, CO and CO_2 or from hydrogen and CO only. Methanol from the second reactor can be used as fuel, synthesis chemical or as feed in methanol powered fuel cells.

Fig. 13, shows a process which comprises of a catalytic permreactor applied in the catalytic dehydrogenation of C_1-C_4 or higher alkane hydrocarbons and takes place within the intermediate catalytic annular space. In the two adjacent tubes a hydrogenation reaction is taking place by using the hydrogen permeated via the membrane tubes. Instead of dehydrogenation reaction, steam or CO_2 reforming of hydrocarbons or water gas shift can take place to produce the permeate hydrogen.

A similar process can be applied in same figure 13 for methane oxidation to synthesis gas. The oxidation catalyst is placed in the inner and outer tubes, and in the empty annular space within, oxygen or air is flowing continuously. The process uses solid oxide type membranes which allow oxygen ions to permeate through the membranes, inside the tubes and react with methane to form synthesis gas.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Fig.1 shows the top cross section of the double wall membrane reactor (permreactor) used in the process of steam and carbon dioxide reforming of hydrocarbons, steam reforming of alcohols, water gas shift and alkane dehydrogenation reactions. It consists of a concentric double membrane wall cylindrical assembly with tubular type heaters located within the catalyst, along the main catalyst zone. An outer impermeable tube (7) nests the two permeable concentric tubes (1) and (2). Reacting feedstocks such as steam and hydrocarbons, CO_2 and hydrocarbons, steam, CO_2 and hydrocarbons, steam and alcohols, or alkanes such as ethane, propane, n-butane, i-butane,

pentane, naphtha and higher paraffins, are fed within the main catalyst zone (4) through special inlet fittings and react in the catalyst to produce hydrogen, carbon monoxide, carbon dioxide. Optionally, small volumetric quantities of hydrogen can be added into above feedstocks to prevent the deactivation of catalyst in the inlet of the reactor, wherein propensity for hydrocarbon cracking into carbon is high in the absence of hydrogen. The hydrocarbon reforming catalysts can be nickel, ruthenium, rhodium, palladium, platinum, iridium enriched with earth type metals such as potassium, calcium, magnesium, lanthanum, cerium, and supported on alumina, silica, titania, zirconia or other inorganic oxides. For the water gas shift reaction the catalytic metals can be nickel, iron, copper, zinc, chromium, cobalt enriched with similar earth metals and supported on similar metal oxides. The methanol reforming catalysts can be zinc, chromium, copper, iron, nickel, ruthenium, rhodium, palladium supported on similar metal oxides. Finally, the described permreactor is applied as well for alkane dehydrogenation reactions and it becomes a catalytic dehydrogenator which utilizes platinum, chromium, palladium catalysts enriched with and supported on similar inorganic oxides.

Hydrogen is removed first along the inner membrane tube (2), wherein the membrane material can be a dense metal, a porous or non-porous inorganic, a porous or non-porous inorganic-metal, another porous or non-porous composite material. Carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols may also permeate through first membrane (2) in a lesser degree than hydrogen if the membrane is made by a porous material. An inert carrier gas such as argon, nitrogen, steam or a mixture of these gases may also flow along the permeate annulus, between tubes (2) and (1), through suitable inlet fittings, to carry the permeate components at a fixed pressure. Permeate hydrogen is further removed via permeation along the outer membrane tube (1), so that permeated stream contains pure hydrogen only, with pure hydrogen to be used in various applications including feed to synthesis reactors, gas turbines and engines, and fuel cells. Outer membrane tube (1) can be made by a dense metal, non-porous inorganic, or composite membrane which allows only hydrogen to permeate through, and therefore purifies hydrogen from the permeating carbon oxides, steam and hydrocarbons, flowing in the annular zone between the two membrane tubes.

Metal materials permeable to hydrogen for the membrane tubes (1) and (2), include palladium, vanadium, palladium alloys such as palladium-nickel, palladium-silver, palladium-zinc, palladium-chromium, palladium-copper, palladium-tungsten and others. Hydrogen permeable non-porous inorganic membranes include silicon carbide, silicon nitride, tungsten carbide, tungsten nitride, titanium carbide, titanium nitride, tantalum carbide, tantalum nitride and others. Porous inorganic membranes include oxides of alumina, silica, titania, zirconia, various types of glass and others. Composite type membranes are made by deposition or fabrication of a metal into a porous inorganic substrate (support) to make it hydrogen permeable. Metal and metal alloys can be deposited on porous inorganic or metal surfaces to make them hydrogen permeable. Palladium and other metal deposited membranes can be fabricated by electroless plating, electroplating, sputtering, chemical vapor deposition, physical vapor deposition and other applicable metal deposition or metallization techniques. Inorganic or inorganic-metal membrane materials can be deposited as well in porous inorganic or metal surfaces (e.g.,

tubes) via various deposition techniques including incipient wetness, dip coating and sol gel methods.

Organic polymer, composite, or copolymer membranes can be made by polymers such as polyimides, polycarbonates, polysulfones, polybenziimidazoles, polyphosphazenes, polyamides, polystyrenes, polycaprolactams, parylenes, polyvinyl halides, polyacetates, polysiloxanes and others in order to be permeable to hydrogen or to hydrogen and carbon dioxide. Finally, composites of the previous materials can be also made as hydrogen permeable membranes such as inorganic-metal, inorganic-organic, inorganic-metal-organic composites. Metal, metal alloy, non-porous inorganic, and types of composite membranes are highly selective to hydrogen, while porous inorganic, organic, and some types of composite membranes are also selective to other species as well. The disclosed double wall permreactor process can utilize among the aforementioned materials to satisfy the consequent process requirements.

The external space, created between the outer membrane tube (1) and the impermeable far outer shell (7), which receives the final permeate hydrogen, can be either empty, or may contain a selective catalyst (5) which converts the permeate hydrogen after its combination with another component flowing via this external space. Such a flowing (sweep) component can be an unsaturated hydrocarbon (e.g., alkenes, alkynes) for conversion to saturated hydrocarbons after combination with hydrogen, in an exothermic reaction. Flowing (sweep) component can be also carbon monoxide for direct production of methanol or hydrocarbons (through Fischer-Tropsch synthesis) after combination with permeate hydrogen in also exothermic type reactions. Flowing gas can be nitrogen for exothermic ammonia synthesis after its combination with the permeate hydrogen. Other combination reactions of flowing compounds with permeate hydrogen can be these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines.

The heat generated by exothermic reactions in the external shell may be transferred into the inner catalytic reaction zone (1) via the radial direction, thus providing for part of the heat load necessary to drive the endothermic catalytic reactions therein.

Permeation of reaction products through the membrane tubes, especially this of hydrogen through the inner membrane tube (2), shifts the thermodynamic equilibrium conversion of reactant species into the product side and produces excess hydrogen and carbon oxides within the catalytic reaction zone (4). Outer membrane tube (1) thereby, serves as a final permeable medium for the recovery of highly pure hydrogen product for use in hydrogen utilization applications. Outer metal membrane tube (1) serves also as a separation medium for hydrogen out of the central annular zone between the two membrane tubes, so that the partial pressure of hydrogen lowers substantially along the annular zone, and thereby continuous driving force exists for permeation of hydrogen from the catalytic reaction zone (4) into the central annular zone (8).

As an alternative to the invented process and design, for low operating gas reforming and dehydrogenation temperatures (e.g., between 200-400°C) and in the absence of steam as reactant, the inner membrane tube (2) can be made by porous

inorganic or porous inorganic-metal materials and the outer membrane tube (1) can be made by dense high temperature organic materials (i.e., materials having high glass transition temperature, Tg) which are permselective to both hydrogen and carbon dioxide. The last two gases permeate through the inner tube (2) and flow along the central annular zone (8). The recovered mixture of H_2 and CO_2 can be used directly in chemical synthesis applications such as this of alternative methanol synthesis via the reaction: $CO_2+3H_2=CH_3OH+H_2O$, and as direct feed in molten carbonate fuel cells via the overall electrochemical reaction: $H_2+CO_2+1/2O_2 \rightarrow H_2O+CO_2$. Moreover mixtures of H_2 and CO_2 can be converted to CH_4 or CO, if a special application requires, via the methanation or reverse water gas shift reactions respectively as shown below:

$CO_2+4H_2=CH_4+2H_2O$, $CO_2+H_2=CO+H_2O$

The external (outer) membrane (1) serves also as a backup membrane medium in case the inner membrane (2) develops cracks or defects and its permeability to various gases increases. In this case, the outer membrane (1) will selectively separate specific gases based on the selected membrane materials as described above. Moreover, operational and maintenance service for replacing old or damaged membrane tubes and catalysts become easier with the proposed design, because the parts of the permreactor are interconnected properly via top and bottom caps and can be disassembled and assembled accordingly. The top and bottom ends of the tubes are sealed with proper materials to prevent gas flow between the various compartments.

An optional design of the permreactor may include an additional catalytic zone (8) which is created between the inner membrane tube (2) and the outer membrane tube (1) and can be used in various reactions and processes.

Heating of the reformer or reactor is achieved via cylindrical tubes (6) arranged symmetrically around the axial reactor axis and operated in the gas combustion regime by flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with oxygen or air. Unreacted hydrocarbons, carbon monoxide, non-permeate hydrogen or any mixture of these species from the catalytic reformer outlets (4), (5), (8), can be recycled as well into the heating combustion tubes (6). In an alternative heating configuration, a single cylindrical tube having the shape of a tube or a coil is located along the reactor axis in zone (4) and can be operated by using same quality of combusted gases. In a third alternative configuration the symmetrically located tubes in (4) can be replaced by cylindrical electric heaters, heating bars or coils.

Fig.2, shows a lateral sectional view of the permreactor described in Fig.1. The embodiment includes catalyst beds 4, 5 and 8 placed along the different tubular sections of the permreactor. The most inner tube bears inner membrane 2 while next inner tube bears outer membrane 1. The most inner tube includes tubular heating elements A6 along its axial length. Feedstock gases are entered into the permreactor via inlet ports A1 and the product and reactant gases exit via outlet ports A3. Alternative safety outlets A5 are located in the outer shell to discharge excess pressure in case of a sudden increase. Top and bottom caps A2 and A4 close the inlet and outlet of the tubular permreactor system and seal properly the ends of the different tubes by means of proper fittings and seal materials to prevent unwanted gas flow or leak between the tubes.

Fig.3, shows multiple double wall permreactors of those described in Fig.1, but without the far outer impermeable tube (7), which are placed symmetrically inside a larger impermeable tube (A1), to create a multiple tube reactor with a common external area for collecting final permeate hydrogen. The common external area may contain a catalyst (zone 5) wherein a catalytic reaction is conducted.

Fig.4 shows the top cross sectional view of another developed double wall membrane reactor (permreactor) used in the process of steam and carbon dioxide reforming of hydrocarbons, steam reforming of alcohols, water gas shift and alkane dehydrogenation reactions. Overall reactor process consists of a most outer hollow impermeable tube (outer shell) (1) which nests two more concentric hollow permeable tubes, a next inner one (2) and a most-inner (3). Most outer cylinder (1) is made by impermeable metal or alloy such as stainless steel. Next-inner membrane tube (2) is made by a dense metal or a metal alloy, a non-porous or porous inorganic, a non-porous or porous inorganic-metal, or another non-porous or porous composite material which is permeable and selective to hydrogen.

The derived concentric multitube assembly has proper inlet and outlet fittings for feeding the feedstocks and discharging the post-reaction species similar to those described in Fig.1 and Fig.2 above. Inlet and outlet fittings are connected into the ends of the three different tubular cylinders similarly to those shown in Fig.2, to deliver and collect gases flowing through these spaces. Top and bottom caps are also used to seal the ends of the overall reactor. Before the caps are applied and tighten, the annular space between the different cylinders is filled with the appropriate catalyst in pellet or particle form to make the catalytic reaction zones (4), (5) and (8). Proper catalyst is used for each reforming, water gas shift and dehydrogenation reactions. Catalysts used in these reactions are same with those mentioned above in the description of embodiment of Fig.1.

In steam, CO_2 reforming of hydrocarbons, steam reforming of alcohols, water gas shift and alkane dehydrogenation reactions, hydrogen is removed along the next-inner lateral membrane surface (2), with carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols to possibly also permeate through the same membrane surface in a lesser degree than hydrogen depending on the type of the membrane material used. An inert carrier gas such as argon, nitrogen, steam or a mixture of those gases, may flows along the permeate annulus, between tubes (2) and (3), through the inlet fittings, to carry the permeate components at a specific pressure value. Permeate hydrogen is further removed through permeation along the lateral surface of most-inner membrane tube (3) so that final permeate stream contains pure hydrogen only, with pure hydrogen to be used in various subsequent applications including feed to synthesis reactors, gas turbines and engines, and fuel cells.

The most-inner membrane tube (3) is made by a dense metal or metal alloy, non-porous inorganic or composite membrane which allows only hydrogen to permeate through and therefore purifies the hydrogen from the permeating carbon oxides, steam, hydrocarbon and alcohol compounds, flowing in the central annular zone (7). The membranes in tubes (2) and (3) can be made with similar manufacturing techniques as

those described in embodiment of Fig.1. The most-inner membrane tube can be either empty or may contain a selective catalyst (5) which can convert permeate hydrogen after combination with another component flowing through the inner bore of this tube. Such a flowing (sweep) component can be an unsaturated hydrocarbon (e.g., alkenes, alkynes) for conversion to saturated hydrocarbons after exothermic reaction with the permeate hydrogen. Flowing (sweep) gas for hydrogenation can be also carbon monoxide for direct production of methanol or gasoline hydrocarbons (through Fischer-Tropsch synthesis) in also exothermic type reactions. Flowing (sweep) gas can be nitrogen for exothermic ammonia synthesis after combination with the permeate hydrogen. Other combination reactions with permeate hydrogen can be these for reduction of aromatic hydrocarbons, these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines. Alternatively, pure permeate hydrogen can be used as direct feed in hydrogen based turbines and engines, fuel cells, and other power generation equipment. The heat generated by exothermic reactions in the most-inner cylindrical bore, may be transferred radially into the catalytic reaction zone of the outer membrane cylinder, thus providing for part of the heat load necessary to drive the endothermic reactions in catalyst bed (4) which is located between tubes (2) and (1).

Permeation of hydrogen through first inner membrane tube (2), shifts the thermodynamic equilibrium conversion of reactant species to the product side and produces excess hydrogen and carbon oxide products.

Most-inner membrane tube (3) thereby, serves as a final permeable medium for the recovery of highly pure hydrogen for use in hydrogen utilization applications. Most-inner membrane tube (3) serves also as a separation medium for hydrogen out of the central annular zone (7) so that partial pressure of hydrogen lowers substantially along the annular zone, and thereby continuous driving force exists for permeation of hydrogen from the catalytic reaction zone (4) into the central annular zone (7).

As an alternative to the disclosed process and design, for low operating gas reforming and dehydrogenation temperatures (e.g., between 200-400°C) and in the absence of steam as reactant, the inner membrane tube (2) can be made by porous inorganic or porous inorganic-metal materials and the most inner membrane tube (3) can be made by dense high temperature organic materials (i.e., materials having high glass transition temperature, Tg) which are permselective to both hydrogen and carbon dioxide. The last two gases may first permeate through the inner membrane (2) and flow along the central annular zone (7). The recovered mixture of H_2 and CO_2 can be used in the applications already described in embodiment of Fig.1.

The most inner membrane tube (3) serves also as a backup membrane in case first inner membrane (2) develops cracks or defects and its permeability to various gases increases. In this case, the most inner membrane (3) will selectively separate specific gases including hydrogen, based on the selected membrane materials as described above. Operational and maintenance service for replacing old or damaged membrane tubes and catalysts in the described permreactor become easier with the proposed design, because the parts of the permreactor are interconnected properly via top and bottom caps and can be disassembled and assembled accordingly. The top and bottom ends of the

interconnected tubes are sealed with proper materials to prevent gas flow between the various compartments.

An optional design of the permreactor may include an additional catalytic zone (7) which is created between the inner membrane tube (2) and the most inner membrane tube (3) and can be used in various reactions and processes.

Heating of the described reactor is achieved via external heat provision (zone 6). The external to the reformer combustion regime can be fueled by flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with oxygen or air. Unreacted hydrocarbons, carbon monoxide product, non-permeate hydrogen product, or any mixture of these post-reaction species coming out of the outlet connected with the catalyst zone (4), (5) or (7) can be recycled as well into the external combustion-heating zone (6). Optionally, external heating of most-outer tube (1) can be provided by cylindrical type heaters or heating elements in contact with the outer tube.

Fig.5, shows multiple double wall permreactors of those described in Fig.4, which are placed symmetrically, inside a larger impermeable tube (shell) (A1), to create a multiple tube permreactor with a common external heating area (6).

Fig.6, depicts a system of catalytic permreactor with consecutive permeator (or optionally a second permreactor) and optionally another third consecutive reactor, for conducting reforming and gas shift reactions. In Fig.6, stream 1 contains hydrocarbon feedstocks such as methane (CH_4), higher alkanes (paraffins), naphtha, natural gas, mixed with steam and CO_2 and introduced in catalytic permreactor A for conducting simultaneously reactions (1), (2) and (3), or mixed with CO_2 only for conducting reactions (1) and (2). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from hydrocarbon cracking especially in the inlet of permreactor A.

Catalytic permreactor A can be any of the types of permreactors described in the embodiments of Fig.1, Fig.3, Fig.4, and Fig.5 above, with H_2 in the general case to be separated in permeate stream 1b via valve A1. H_2 and CO_2 gases combined can be separated in permeate stream 1b in special applications, if a suitable organic, inorganic, or composite membrane is used in permreactor A. The rejected exit stream from the permreactor may contain CO product together with unreacted steam ($H_2O(g)$), CO_2, hydrocarbons, and non-permeate H_2. This stream becomes stream 2 and enters into a heat exchanger B, wherein the unreacted steam is removed through condensation and by the heat exchanging process new steam is generated in stream 6 from the water or steam of stream 5. Stream 6, can provide steam in permreactor A and reactor E through streams 9 and 10,18 respectively, in an alternative or continuous manner via use of valves B1 and E1. The steam in stream 6 acquires the exchanged heat load from stream 2, the hot gas effluent of reformer A, and thus its derived streams 9,10,18 can be mixed directly with streams 1 and 12 which are fed directly into reactors A and E respectively.

Steam from stream 6 is used via streams 10,18 and valves B1,E1 to provide the initial steam content in reformer E. Stream 7, passes through a bed of particles C (a moisture adsorbent) to remove any non-condensed traces of moisture and through the exit stream 8 enters into membrane permeator D. Stream 8, contains CO product, non-

permeate H_2 product, unreacted hydrocarbon (e.g., CH_4) and CO_2 gases and has been cooled at the operating temperature of permeator D. H_2 or both H_2 and CO_2 are removed in permeate stream 11 of permeator D, through the permselective action of a metal, non-porous inorganic, organic or composite membrane respectively. Non permeating stream 12, containing hydrocarbons (e.g., CH_4), CO and CO_2 or hydrocarbons and CO respectively, depending on the type of membrane used in permeator D, exits from permeator D, through stream 12 as reject stream. Stream 12 enters into reformer E, for conducting simultaneously reforming and water shift reactions selected from the group of reactions (1), (2) and (3), and be converted into final products H_2, CO, CO_2 or H_2 and CO_2 only, depending on the feed composition of stream 12 in reformer E. Steam in reformer E is provided via stream 18. Unreacted steam is removed from exit stream 15 by passing this stream through a heat exchanger F. Steam is generated from water or steam of stream 16 and via streams 17,18 and valve E1, the generated steam is fed into the inlet of reformer E. Exit stream 19 contains H_2, CO, CO_2 or H_2, CO_2 products and traces of unreacted hydrocarbons, depending on the operating conditions, that is the temperature, pressure, space velocity and feed composition of streams 12 and 18, of reformer E. Reformer E, can be replaced by a permeable reformer E similar to permeable reformer A, wherein H_2 is separated in permeate and the reject exit stream 19 consists of CO and CO_2 or of CO_2 only.

Reformers A and E are endothermic and flue gas streams 3,4 and 13,14 respectively are used to provide the necessary heat content to drive parallel reactions (1), (2) and (3) to completion. The two reformers can operate at same or different temperature and pressure conditions.

If conversion is high in permeable reformer A under certain operating conditions, the product in stream 2 is mainly CO and H_2 which can be used directly as synthesis gas in methanol synthesis via the direct exothermic reaction: $CO+2H_2=CH_3OH$, also in Fischer-Tropsch type reactions for production of gasoline type hydrocarbons, and as fuel in gas turbines and engines and solid oxide fuel cells for power generation.

If the overall process consists of two reformers and the intermediate permeator, and the final product is a H_2 and CO_2 mixture in exit stream 19, it can be used separately or it can be mixed with stream 11 to make a combined H_2 and CO_2 stream. This combined H_2, CO_2 mixture can be used for direct methanol synthesis via the exothermic reaction: $3H_2+CO_2=CH_3OH(g)+H_2O(g)$. Also, the H_2, CO_2 mixture can be used as direct feed in molten carbonate fuel cells for electricity generation via the overall electrochemical reaction:

$H_2+CO_2+1/2O_2$ (cathode) $\dashrightarrow H_2O+CO_2$ (anode)

Alternatively, CO_2 can be condensed cryogenically from the binary mixture and pure hydrogen can be produced. Final H_2 product can be used for chemical synthesis or as direct feed in fuel cells and gas turbines and engines for power generation applications (e.g., transportation, stationary). Applicable hydrogen driven fuel cells for utilizing the pure separated hydogen from the process, include proton exchange membrane (PEM), solid oxide (SOFC), molten carbonate (MCFC), alkaline (AFC), phosphoric acid (PAFC) and modifications and combinations of these fuel cells.

Generated hydrogen product from the process can be combined with an unsaturated hydrocarbon (e.g., alkenes, alkynes) for conversion to saturated hydrocarbons

in an exothermic type reaction. Also, with carbon monoxide for direct production of methanol (as described above) or gasoline (through Fischer-Tropsch synthesis) in exothermic type reactions. Hydrogen can be also combined with nitrogen for exothermic ammonia synthesis. Other combination (synthesis) reactions with permeate hydrogen can be these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines.

The described process is able to overcome the thermodynamic equilibrium limitations of hydrocarbon (CH_4) and CO_2 reactant conversion, through the removal of H_2 only, or of H_2 and CO_2 gases in permreactor A and permeator D. The calorific value of the obtained H_2, CO product in permreactor A, is higher than this of the reactant hydrocarbon (e.g., CH_4), CO_2 and steam and the endothermic heat of reaction is stored in the products which can be subsequently used as fuels or in chemical synthesis.

Assuming 100% conversion of reactions (1) and (2) and reaction (3) in equilibrium in permreactor A, 2 mol of CH_4 (with heat of combustion: 425.6 kcal), 1 mol of CO_2 (with no heat of combustion), and 1 mol of $H_2O(g)$ (with no heat of combustion), produce 3 mol of CO (with heat of combustion: 202.8 kcal) and 5 mol of H_2 (with heat of combustion: 341.5 kcal). These values are at 25°C. This corresponds to about 28% increase in calorific value for the product. Endothermic heat can be provided in reformers A and E through the combustion of flue or waste gases or unreacted recycled hydrocarbons coming out of the exit of reaction zone of reformers A and E (such as streams 7, 12, 19) as also described in Figs.1, 2, 3, 4, 5 above.

In an alternative design, permeator D is replaced by a catalytic permreactor D wherein the water gas shift reaction occurs if stream 8 is rich in product CO. In such a case permreactor D is made by metal, non-porous inorganic, or composite membranes to separate only hydrogen in permeate stream 11. Exit reject stream 12 from permreactor D contains product CO_2 and unreacted steam and can be recycled in the first reforming permreactor A or used in downstream applications either as a mixture or as pure CO_2 after condensation of the steam.

Fig.7, describes an embodiment similar to the one described in Fig.6, but the inlet stream 1 contains carbon monoxide (CO) only mixed with steam and introduced in catalytic permreactor A which is filled with catalyst particles to conduct the water gas shift reaction only.

Catalytic water gas shift permreactor A, can be any of the types of permreactors described in the embodiments of Fig.1, Fig.3, Fig.4, and Fig.5 above, with H_2 in the general case to be separated in permeate stream 1b via valve A1. H_2 and CO_2 gases combined can be separated in permeate stream 1b for special applications, if an organic, inorganic, or composite membrane is used in permreactor A. The rejected exit stream from the permreactor contains product CO together with unreacted steam ($H_2O(g)$) and non-permeate H_2. This becomes stream 2 and enters into a heat exchanger B, wherein the unreacted steam is removed through condensation, and by the heat exchanging process new steam is generated in stream 6 from the water or steam of stream 5. Stream 6, can provide steam in permreactor A and reactor E through streams 4 and 11, 13 respectively,

in an alternative or continuous manner via use of valves B1,F1. The steam in 6 aquires the exchanged heat load from stream 2, the hot gas effluent of permeable reactor A, and thus its derived streams 4,11,13 can be mixed directly with streams 1 and 12 which are fed directly into reactors A and E respectively.

Steam from stream 6 is used via streams 11,13 and valve F1 to provide initial steam in reactor E. Stream 7 passes through a bed of particles (a moisture adsorbent) C to remove any non-condensed traces of moisture and through exit stream 8 enters into membrane permeator D. Stream 8 contains non-permeate product H_2, product CO_2 and unreacted CO gases and has been cooled at the temperature of permeator D. H_2 and CO_2 are removed in permeate stream 9 through permselective action of membrane in permeator D. Non permeating CO exits from permeator through stream 10 which can be called a reject stream. Stream 10 can be recycled via valve D1 as stream 3 into the first permeable shift reactor A for contiuous shift reaction and conversion to H_2 and CO_2 products. Alternatively, by use of same valve D1, stream 10 becomes 12 which enters into reactor E for additional water gas shift reaction, and conversion into final H_2, CO_2 products. Unreacted steam is removed from exit stream 14 by passing this stream through heat exchanger F. New steam is generated from water or steam of stream 15 and via streams 16,13 and valve F1 is fed into inlet of reactor E. Exit stream 17 contains H_2, CO_2 products and traces of unreacted CO depending on the operating conditions, that is the temperature, pressure, space velocity, and feed composition of streams 12 and 13 of reactor E.

Shift reactors A and E are exothermic and no heat input is necessary as with the previous endothermic reformers described in previous embodiments. Stream 1 needs to be preheated in temperature of permeable reactor A before entering into reactor. Using the heat content of streams 2 and 14 exiting from the reactors to provide the necessary heat content in the feed streams 4 and 13 entering into the reactors, the entire process operates in an autothermic way with no additional heat input necessary. The two shift reactors can operate at same or different temperature and pressure conditions.

Exit stream 17 can be used separately or it can be mixed with stream 9 to make a combined H_2 and CO_2 stream to be used for chemical synthesis or as fuel in applications similar to the ones mentioned in Fig.6. Pure H_2 from the process can be recovered after the CO_2 condensation and removal. Pure hydrogen from the process, can be used as fuel or in chemical synthesis applications, as described in embodiment of Fig.6 above.

The described shift process can overcome the equilibrium CO reactant conversion through removal of the H_2 in permreactor A and the intermediate removal of H_2 and CO_2 products in permeator D. Thus, the process can increase the CO conversion and the H_2, CO_2 yields above the values obtained with conventional water gas shift reaction systems. By use of the two heat exchangers each shift reactor operates in an autothermic way with no need of additional heat load in the system except for the initial preheating of stream 1 to start-up operation in permreactor A.

Fig.8 is an embodiment of a system of catalytic permreactor with consecutive permeator for conducting alkane (paraffin) dehydrogenation reactions. In Fig.8, stream 1 contains hydrocarbon feedstocks such as ethane, propane, n-butane, i-butane, naphtha, or liquid alkanes such as pentane, hexane, heptane. Liquid alkanes are vaporized by

preheating before fed into the catalytic membrane dehydrogenator A. Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation in the catalyst from hydrocarbon cracking especially in the inlet of permreactor A.

Catalytic permeable dehydrogenator A, can be any of the types described in embodiments of Figs.1, 3, 4, 5 above, with H_2 to be separated in permeate stream 1b via valve A1. The rejected exit stream from permreactor A contains unreacted paraffins, product olefins, and non-permeate hydrogen. This becomes stream 2 and optionally passes through a heat exchanger B, wherein by the heat exchanging process steam is generated in stream 6 from the water or steam of stream 5 to be used in steam requiring applications.

Stream 7, enters into membrane permeator C. H_2 is removed in permeate stream 8 of permeator C, through the permselective action of a metal, non-porous inorganic, composite, or organic membrane. Non permeating stream 9 containing hydrocarbons (product olefins and traces of unreacted paraffins) exits from permeator C as reject stream. Stream 9 has composition dependent on the paraffin conversion in permreactor A and the hydrogen separation efficiency in permeator C. By optimizing these two parameters, pure olefins can be produced in stream 9, to be used as direct feed in polyolefin production reactors E for polyolefin production (i.e., polyethylene, polypropylene) with the final polymer product to exit from stream 10. Olefins from stream 9 are also used as direct feed in synthesis reactors, such as ethylene for ethylene oxide and ethylene glycol production, propylene for propylene oxide and propylene glycol production, isobutylene for MTBE production used as blending in reformulated gasoline. Produced pure hydrogen from the described process can be used within the same fuel utilization and synthesis applications as described in embodiments of Figs.1 and 5.

Paraffin dehydrogenation reactions are endothermic, and reactor A receives heat from flue gas streams 3,4 to drive dehydrogenation reactions (4) to completion.

The described process is able to overcome thermodynamic equilibrium limitations for paraffin conversion met in conventional reactors, through the removal of H_2 product in membrane permreactor A and permeator C. Endothermic heat can be provided in dehydrogenator A through the combustion of flue or waste hydrocarbons or unreacted recycled hydrocarbons from the reaction zone of reactor A as also described in embodiments of Figs.1,3,4, and 5 above.

Permeable dehydrogenator A can be substituted by a non-permeable (e.g., non-porous stainless steel wall) dehydrogenator A. Valve A1 and stream 1b are eliminated and all post-reaction gases exit from stream 2. Permeator C still operates with the same function as described above.

In an alternative process, permeator C can employ a specific polymer-metal or composite membrane for separation of the produced olefins from the unreacted paraffins. In this case the olefin rich stream exits via permeate stream 8, and the reject stream 9 rich in unreacted paraffins is recycled into permreactor A. Such membranes can be made by polymers dispersed with metals such as copper (Cu), silver (Ag), zinc (Zn), chromium (Cr), cobalt (Co), nickel (Ni).

Fig.9, is an embodiment which is related with those described in Figs.6 and 7, but with stream 1 to contain hydrocarbon feedstocks such as methane or higher alkanes such as naphtha and natural gas, also alcohol feedstocks such as methanol, ethanol, propanol, butanol mixed with steam only and introduced in catalytic permreactor A which is filled with catalyst particles to conduct the methane steam reforming reaction (1) and the simultaneously occurring water gas shift reaction (3). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from hydrocarbon cracking especially in the inlet of permreactor A.

Catalytic permreactor A, can be any of the reactor types described in embodiments of Figs.1,3,4,5 above, with H_2 to be separated in permeate stream 1b via valve A1, in the general case. H_2 and CO_2 combined, can be separated in permeate stream 1b in special applications, if an organic, inorganic, or composite membrane is used in permreactor A. The rejected exit stream from the permreactor may contain product CO_2, CO, unreacted steam ($H_2O(g)$), hydrocarbons, and non-permeate H_2. This becomes stream 2 and enters into heat exchanger B, wherein the unreacted steam is removed through condensation, and by the heat exchanging process new steam is generated in stream 8 from the water or steam of stream 7. Stream 8, can provide steam in permreactor A and reactor E through streams 6 and 10,20 respectively, in an alternative or continuous manner via use of valves B1,E1. The steam in 8 aquires the exchanged heat load from stream 2, the hot gas effluent from permeable reformer A, and thus its derived streams 6,10,20 can be mixed directly with streams 1 and 14 which are fed directly into reactors A and E respectively.

Steam from stream 8 is used via streams 10,20 and valve E1 to provide the initial steam in reformer E. Stream 9 passes through a bed of particles (a moisture adsorbent) C to remove any non-condensed traces of moisture and through exit stream 11 enters into membrane permeator D. Stream 11 has been cooled in temperature of permeator D and contains CO, CO_2, unreacted hydrocarbons, and non-permeate H_2 gas species.

H_2 or both H_2 and CO_2 are removed via permeate stream 12 of permeator D, through the permselective action of a metal, non-porous inorganic, composite or organic membrane. Non permeating stream 13 containing hydrocarbons (e.g., CH_4), CO and CO_2 or hydrocarbons and CO respectively, depending on the type of the membrane used in permeator D, exits from permeator D, through the reject stream 13. In case wherein stream 13 contains hydrocarbons and carbon monoxide (CO) it can be recycled via valve D1 and stream 5 into first permeable reformer A for continuous reforming and conversion to main H_2 and CO_2 products. Alternatively, by use of valve D1, stream 13 becomes stream 14 which enters into steam reformer E for additional reforming and shift reactions, (reactions (1), (3)), and conversion to H_2 and CO_2 products. In case wherein stream 13 contains hydrocarbons, CO and CO_2, by use of valve D1, stream 13 becomes stream 14 which enters into modified steam and CO_2 reformer E for additional reforming and shift reactions, via reactions (1), (2) and (3) and conversion into H_2, CO, CO_2 products. Reformer E, can be replaced by a permeable reformer E similar to permeable reformer A, wherein H_2 is separated in permeate and the reject exit stream 17 consists of product CO and CO_2.

Reformers A and E are endothermic and flue gas streams 3,4 and 15,16 respectively are used to provide the necessary heat content to drive parallel reactions (1), (2) and (3) to completion. The two reformers can operate at same or different reaction temperature and pressure conditions.

If conversion is high in permeable reformer A under certain operating conditions, the product in stream 2 is mainly CO_2 and non-permeate H_2 which can be used directly in H_2, CO_2 applications described already in embodiment of Figs. 1 and 4.

If the overall process includes a second conventional reformer E and the intermediate permeator as shown in Fig.9, and final product is H_2 and CO_2 in exit stream 21, this product can be used separately or it can be mixed with stream 12 to make a combined H_2 and CO_2 stream to be used in similar applications. Alternatively, CO_2 can be condensed cryogenically from the binary mixture and pure hydrogen product can be produced. Final H_2 product can be used for chemical synthesis or as direct feed in fuel cells, gas turbines and engines for power generation applications (e.g., transportation, stationary), same to those described in embodiments of the previous figures.

The described process is able to overcome thermodynamic equilibrium limitations of hydrocarbon (e.g., CH_4) and steam reactant conversion, through the removal of H_2 product only, or of the combined H_2 and CO_2 products in membrane permreactor A and permeator D. The calorific value of the obtained H_2 and CO_2 products in permreactor A is higher than this of the reactant hydrocarbon (e.g., CH_4) and steam mixture, because the provided endothermic heat of reaction is stored in the products and can be subsequently released by using products as fuels or in chemical synthesis.

Assuming 100% conversion of reactions (1) and (3), 1 mol of CH_4 (with heat of combustion: 212.8 kcal) and 2 mol of $H_2O(g)$ (with no heat of combustion) generate 1 mol of CO_2 (with no heat of combustion) and 4 mol of H_2 (with heat of combustion: 273.3 kcal). These values are at 25°C. This corresponds to about 28% increase in calorific value for the product gases. By providing external heat through flue or waste gas combustion in the reformers or through internal stream recycling and with the described two heat exchangers in place, the energy requirement of the one reactor-one permeator or two reactor-one permeator cascades is fulfilled and these processes operate in a thermally independent manner providing for an energy efficient design. Endothermic heat can be provided also in reformers A and E via the combustion of exit or recycled streams from the reaction zone of reformers A and E (streams 9, 13, 21), as also described in Figs.1,2,3,4,5 above.

Fig.10, is an embodiment of a steam and CO_2 hydrocarbon reforming process which includes a permeable reformer or a non-permeable reformer followed by a cryogenic separator for separation of certain post-reaction gases exiting from the reject exit of the reformer. In Fig.10, stream 1 is introduced into catalytic permreactor A, containing hydrocarbon feedstocks such as methane (CH_4) mixed with steam and CO_2 for conducting simultaneously reactions (1), (2) and (3), or mixed with CO_2 only for conducting reactions (1) and (2). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from methane cracking especially in the inlet of permreactor A.

Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with H_2 to be separated from the reformer, and exit in permeate stream 1b via valve A1. The rejected exit stream from the permreactor contains product CO together with unreacted steam ($H_2O(g)$), CO_2, and hydrocarbon, and non-permeate H_2. This becomes stream 2 and enters into a steam condenser C wherein the unreacted steam is condensed and by the heat exchanging process new steam is generated in steam 17 from the water or steam of stream 16. Steam through stream 17 is recycled into stream 1 in inlet of reformer A. Stream 5 free of steam, exits from condenser C and enters into cryogenic separator B, which operates at a temperature lower than the boiling temperature of carbon dioxide and hydrocarbons so that these compounds are separated easily as liquids and collected in the bottom of the separator (the operating cryogenic temperature of the separator is a negative number which has larger absolute value than the absolute value of any of the boiling points of the liquified components above). However, the operating cryogenic temperature of separator is higher than the boiling points of carbon monoxide and hydrogen so that these compounds remain in gas phase and exit from the separator as a gas mixture (operating cryogenic temperature of the separator is a negative number which has smaller absolute value than the absolute value of the boiling points of both hydrogen and carbon monoxide). Liquified components exit via stream 7 through valve B1. Gas phase hydrogen and carbon monoxide exit as stream 6 via valve B2. Liquified stream 7 can be recycled into the feed stream of reformer A (stream 1) via stream 8 after evaporation in evaporator D. Alternatively, stream 7 can be further processed in another reforming reactor by becoming stream 9 which enters into reformer E, for additional steam and CO_2 reforming of any remaining hydrocarbons via reactions (1), (2) and (3). Optionally, steam in reformer E is provided via stream 18 which is a bypass stream of stream 17. Stream 10 exiting the reformer can optionally condense the containing unreacted steam by passing through the heat exchanger F. Inlet stream 11 contains water which becomes steam in stream 12 after passing through F. Steam in stream 12 can optionally fed into reformer E via valve E1. Stream 13 exiting the heat exchanger F is dry, and contains H_2 and CO as main products with traces of unreacted hydrocarbons and CO_2 depending on the operating temperature and pressure of the reformer E and the composition of feed streams 9 and 12.

Recovered H_2 and CO in stream 13 can be either used separately or optionally be combined with stream 6 from the separator to make one stream to be used as fuel in conventional and fuel cell systems or in chemical synthesis. Direct application of the produced H_2 and CO mixture is in methanol synthesis via the direct exothermic reaction: $CO+2H_2=CH_3OH$, also in Fischer-Tropsch type reactions for production of gasoline type hydrocarbons, as fuel in gas turbines and engines and solid oxide fuel cells for power generation. Similarly, H_2 recovered in stream 1b, can be used as fuel or in chemical synthesis, as described in previous embodiments. The described process is able to overcome the thermodynamic equilibrium limitations of hydrocarbon (e.g., CH_4), steam, and CO_2 reactant conversion, through the removal of H_2 and H_2 and CO gases in membrane permreactor A and cryogenic separator B respectively. Endothermic heat in reformers A and E is provided through gas streams 3,4 and 14,15 respectively. Streams 3, 14 can be fed by a bypass stream of exit stream 2, as also described in embodiments of previous figures. The reformer A can be optionally substituted by a non-permeable

reformer A, wherein stream 1b and valve A1 are eliminated and all product H_2 is included in post-reaction mixture entering through the stream 2 into cryogenic separator B.

Fig.11, is a modified embodiment of the process described in Fig.6. It applies to a complete conversion of hydrocarbons (e.g., CH_4) and CO_2 reactants of stream 1, within the permeable reformer A, to H_2 and CO products. The occurring reactions are (1),(2),(3) or (1),(2) only. Catalytic permreactor A, can be any of the types described in embodiments of Figs. 1,3,4 and 5 above, with H_2 to be separated in permeate stream 3 via valve A1. The exiting from the permreactor, stream 2, containing only CO and non-permeating H_2, or CO, non-permeating H_2, and traces of unreacted steam, enters into a solid oxide fuel cell (SOFC) which is unit B. Stream 2 is directed in the anode of the solid oxide cell, and consists the fuel constituent of the fuel cell. O_2 in stream 4, is directed in the cathode of the fuel cell and consists the oxidant, for the well known electrochemical reaction conducted within the cell with electric current generation:

In Anode: $H_2 + O^{2-} \dashrightarrow H_2O + 2e^-$

$CO + O^{2-} \dashrightarrow CO_2 + 2e^-$

In Cathode: $O_2 + 4e^- \dashrightarrow 2O^{2-}$

Optionally, part of hydrogen from permeate stream 3, can be fed into stream 2, via bypass stream 3b, to adjust the composition of H_2 in stream 2 to that required to feed the fuel cell B. Flue gas streams 5 and 6, are used to provide the endothermic heat content into the reformer A. Stream 5 can be fed by a bypass stream of exit stream 2, as also described in embodiments of Figs.1,3,4,5. The reformer A can be optionally substituted by a non-permeable reformer A, wherein all product H_2 is included in exit stream 2. Valve A1 and streams 3 and 3b are eliminated and all post-reaction gases exit from stream 2. Fuel cell B still operates in same function as described above.

Fig.12, is a modified embodiment of the process described in Fig.6. It pertains to methanol production from the products of the reforming reaction occurring in permreactor A, and the subsequent utilization of methanol in a methanol fuel cell. The process describes the complete conversion of hydrocarbons (e.g., CH_4) and CO_2 reactants, in stream 1, within the permeable reformer A, into H_2 and CO products. The occurring reactions are (1),(2),(3) or (1),(2) only. Catalytic permeable reformer A, can be any of the types described in embodiments of Figs. 1,3,4, and 5 above, with H_2 to be separated in permeate stream 1b via valve A1. The exiting from the permreactor, stream 2, containing only CO and non-permeating H_2, or CO, non-permeating H_2, and traces of unreacted steam, passes through heat exchanger B and moisture adsorbent C to remove unreacted steam and result in an all dry stream of H_2 and CO. Stream 8, of H_2 and CO products (synthesis gas) enters into the methanol synthesis reactor D, wherein methanol is produced via the following exothermic reaction: $CO+2H_2=CH_3OH$, ΔH^o_{298}=-128.2kJ/mol (13.1). Reactor D, can be a slurry type reactor or a catalytic plug flow reactor with methanol to be produced in gas or liquid phase depending on the temperature, pressure and feed composition into the reactor and the type of catalyst used. Zinc, copper and chromium oxide catalysts are well known to convert synthesis gas to

methanol. Methanol from stream 9 can be fed into a methanol driven fuel cell for electricity generation or for further use as a synthesis chemical.

Optionally, stream 1c, which is a bypass stream of stream 1b and contains pure hydrogen, can be recycled into stream 8 via stream 16 to adjust hydrogen composition in this stream where necessary, and to increase the efficiency of methanol synthesis in reactor D. Product hydrogen from stream 1b can be used in fuel, fuel cell, and synthesis applications. Reformer A is endothermic and flue gas streams 3,4 are used to provide the necessary heat content to drive parallel reactions (1), (2), (3) to completion. Stream 3 can be fed by a bypass stream of stream 1 or 2. Optionally, reformer A can be a non-permeable reformer with only one post-reaction outlet (exit), this of stream 2, which delivers all products and unreacted reactants into the heat exchanger B and next into methanol reactor D.

Fig.13, is a modified embodiment of the process described in Fig.4. It shows a cross section of a similar concentric double wall permreactor, consisting of an outer impermeable tube, a next-inner and a most-inner membrane tubes with the two later ones to be made by metal, inorganic, or composite membranes to be used for hydrogen permeation. Hydrogen is generated by conducting dehydrogenation and steam, CO_2 reforming type reactions within the catalyst located in the central annular zone. Two additional catalytic zones are created by filling the space between outer and next-inner tubes and in most inner tube with suitable metallic catalyst, so that corresponding hydrogenation reactions take place in the catalyst by utilizing the permeate hydrogen. The central annular zone includes tubular type heaters running along the axial direction.

The same modified double membrane reactor structure can be applied to the oxidation of methane and to the methane oxidative coupling reactions for production of synthesis gas or higher hydrocarbons respectively. In this case, both membrane tubes are made by solid oxide, oxygen ion-conducting materials which are permeable to oxygen or air. Oxygen or air permeate and react with methane to make final products in the inner and outer catalytic annular zones which are filled with suitable metal and metal oxide catalysts. The central annular zone is empty in this case and no heating or heaters are required within because the reactions are exothermic.

We claim:

1. A process for conducting catalytic steam and CO_2 hydrocarbon reforming, steam-alcohol reforming, water gas shift, and dehydrogenation reactions for production and use of hydrogen and synthesis gas which includes:

a far-outer impermeable hollow tubular cylinder which nests two more concentric permeable tubular cylinders, having the inner permeable one to be nested within the outer permeable cylinder, with the inner permeable cylinder to be filled with catalyst particles and include tubular type heaters located along the axis, with the catalyst in